

Substitute Specification

TITLE OF THE INVENTION

[0001] Vinyl-Cis-Polybutadiene Rubber and Butadiene Rubber Composition Using the Same  
CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This application is a continuation of International Application No. PCT/JP2004/018417,  
5 filed December 2, 2004, which was published in the Japanese language on June 23, 2005, under  
International Publication No. WO 2005/056663 and the disclosure of which is incorporated herein  
by reference.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to a novel vinyl-cis-polybutadiene rubber produced by  
10 concurrently allowing 1,2-polybutadiene of a high melting point of 170°C or more and polyisoprene  
or polybutadiene of a low melting point to exist and be dispersed in the matrix of cis-polybutadiene  
rubber. Further, the invention relates to a butadiene rubber composition using the vinyl-cis-  
polybutadiene rubber.

[0004] In the molecular chain of polybutadiene, a binding portion generated by 1,4  
15 polymerization (1,4 structure) and a binding portion generated by 1,2 polymerization (1,2 structure)  
concurrently exist as so-called microstructure. The 1,4 structure is divided in two types of structures,  
namely cis structure and trans structure. Alternatively, the 1,2 structure takes a structure with vinyl  
group as a side chain.

[0005] A method for producing vinyl-cis-polybutadiene rubber composition in the related art has  
20 been carried out in inert organic solvents such as aromatic hydrocarbons such as benzene, toluene  
and xylene and halogenated hydrocarbons thereof for example chlorobenzene. When solvents such  
as aromatic hydrocarbons and halogenated hydrocarbons are used, however, the resulting  
polymerization solution has such a high viscosity that the agitation, heat transmission and transfer  
thereof are troublesome, which requires excessive energy for the recovery of such solvent.

25 Additionally, solvents such as aromatic hydrocarbons and halogenated hydrocarbons are very  
hazardous for environment, due to the toxicity and carcinogenesis.

[0006] As the production method, a method including a step of producing cis-polybutadiene  
rubber by cis-1,4 polymerization of 1,3-butadiene using a catalyst obtained from water, a soluble  
cobalt compound and an organic aluminum chloride represented by the general formula  $AlR_nX_{3-n}$   
30 (provided that R is an alkyl group with one to 6 carbon atoms, phenyl group or cycloalkyl group; X

is a halogen element; and n is a numerical figure of 1.5 to 2) in the inert organic solvent, and a step of syndiotactic 1,2 polymerization (abbreviated as "1,2 polymerization" hereinafter) of 1,3-butadiene in the presence of a syndiotactic 1,2 polymerization catalyst obtained from a soluble cobalt compound, an organic aluminum compound represented by the general formula  $AlR_3$  (provided that R is an alkyl group with one to 6 carbon atoms, phenyl group or cycloalkyl group) and carbon disulfide, with addition or no addition of 1,3-butadiene and/or the solvent to the resulting polymerization system is known (see for example JP-B-49-17666 (patent reference 1) and JP-B-49-17667 (patent reference 2)).

[0007] Additionally, for example, JP-B-62-171 (patent reference 3), JP-B-63-36324 (patent reference 4), JP-B-2-37927 (patent reference 5), JP-B-2-38081 (patent reference 6), and JP-B-3-63566 (patent reference 7) describe methods including a step of producing vinyl-cis-polybutadiene rubber composition by cis-1,4 polymerization of 1,3-butadiene in the presence or absence of carbon disulfide, and methods including a step of separating and recovering 1,3-butadiene and carbon disulfide to recycle 1,3-butadiene substantially never containing carbon disulfide and the inert organic solvent. Further, JP-B-4-48815 (patent reference 8) describes a rubber composition with a small die swell ratio of compounded material, of which the vulcanized product has an excellent tensile strength and a great flex-crack-growth resistance preferable as the sidewall of tire.

[0008] Additionally, JP-A-2000-44633 (patent reference 9) describes a method for producing vinyl-cis-polybutadiene rubber in an inert organic solvent containing  $C_4$  distillates such as n-butane, cis-2-butene, trans-2-butene, and butene-1 as the main components. JP-A-2000-44633 describes that 1,2-polybutadiene contained in the rubber composition according to the method is a crystal in short fiber, where 98 % or more of the fiber length is less than  $0.6\ \mu m$  in the distribution of the crystal in short fiber along major axis; and 70 % or more thereof is less than  $0.2\ \mu m$  and that the resulting rubber composition has improved moldability of cis-1,4-polybutadiene, tensile stress, tensile strength and flex-crack-growth resistance.

[0009] However, a rubber composition with improved various properties has been demanded for some use.

Patent Reference 1: JP-B-49-17666

Patent Reference 2: JP-B-49-17667

Patent Reference 3: JP-B-62-171

Patent Reference 4: JP-B-63-36324

Patent Reference 5: JP-B-2-37927

Patent Reference 6: JP-B-2-38081

Patent Reference 7: JP-B-3-63566

Patent Reference 8: JP-B-4-48815

Patent Reference 9: JP-A-2000-44633

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## BRIEF SUMMARY OF THE INVENTION

[0010] It is an object of the invention to provide vinyl-cis-polybutadiene rubber giving a butadiene rubber composition with a small die swell ratio and excellent extrusion processability and operability for producing tire, which exerts excellent break-resistant properties, abrasion resistance and sliding friction resistance as well as very great flex-crack-growth resistance and high rigidity, when the butadiene rubber composition is vulcanized. It is an object of the invention to provide a butadiene rubber composition with the excellent properties, particularly a butadiene rubber composition for tire.

[0011] The invention has achieved the objects via the following constitutions.

[0012] 1. A vinyl-cis-polybutadiene rubber containing 1,2-polybutadiene and a polymer substance with a melting point lower than that of the 1,2-polybutadiene and with at least one unsaturated double bond per repeating unit, where the 1,2-polybutadiene and the polymer substance are dispersed at physically and/or chemically adsorbed states in the cis-polybutadiene rubber as the matrix component of the vinyl-cis-polybutadiene rubber.

[0013] 2. The vinyl-cis-polybutadiene rubber described in 1. above, where the 1,2-polybutadiene and the polymer substance are dispersed in short crystal fiber and/or particle in the cis-polybutadiene rubber as the matrix component of the vinyl-cis-polybutadiene rubber.

[0014] 3. The vinyl-cis-polybutadiene rubber described in 1. or 2. above, where the 1,2-polybutadiene is 1,2-polybutadiene of a melting point of 170°C or more and the polymer substance is at least one selected from polyisoprene, crystallizable polybutadiene of a melting point of 150°C or less, liquid polybutadiene and derivatives thereof.

[0015] 4. The vinyl-cis-polybutadiene rubber described in any of 1. through 3. above, where the unsaturated polymer substance is contained within a range of 0.01 to 50 % by mass to the total of the crystal fiber of the 1,2-polybutadiene and cis-polybutadiene rubber.

[0016] 5. The vinyl-cis-polybutadiene rubber described in any of 1. through 4., where the viscosity of the cis-polybutadiene rubber as the matrix component in toluene solution at 25°C is within a range of 10 to 150.